

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 960 918 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
01.12.1999 Bulletin 1999/48

(51) Int. Cl.⁶: **C09D 127/06**, **C09D 133/12**,
C08K 3/22

(21) Application number: **99103674.0**

(22) Date of filing: **25.02.1999**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **05.03.1998 US 35256**

(71) Applicant: **AUSIMONT U.S.A., Inc.**
Thorofare, New Jersey 08086 (US)

(72) Inventors:

- **Lin, Shlow-Ching**
Lawrenceville, New Jersey 08648 (US)
- **Kamsler, Craig**
North Brunswick, New Jersey 08902 (US)
- **Argasinski, Karol**
Sicklerville, New Jersey 08081 (US)

(74) Representative:

Sama, Daniele, Dr. et al
Sama Patents,
Via G.B. Morgagni, 2
20129 Milano (IT)

(54) **Polyvinylidene fluoride weather resistant coating compositions including polymethyl methacrylate**

(57) A coating composition blend comprising PVDF and PMMA with the PMMA having a molecular weight within the range of about 25,000 grams per mole to about 200,000 grams per mole that results in a blend of PVDF and PMMA with excellent physical characteristics, including solvent resistance and gloss retention.

EP 0 960 918 A2

Description

[0001] The present invention relates to a blend comprising polyvinylidene fluoride ("PVDF") and polymethyl methacrylate ("PMMA") comprising PMMA having a molecular weight within the range from about 25,000 grams per mole to about 200,000 grams per mole. The invention provides a blend with superior physical characteristics, including solved resistance and gloss retention. Insofar as the present inventors are aware, a molecular weight range of PMMA in a PVDF/PMMA blend that results in enhanced and excellent physical characteristics, including solvent resistance and gloss retention heretofore has not been identified.

[0002] PVDF has been a very important raw material for architectural coatings based largely on its ultraviolet ("UV") light transparency. PVDF provides long term protection for metal surfaces against exterior exposure, much better than other known coating materials. In order to balance the performance of PVDF coatings, a secondary resin normally is needed to provide good adhesion to a substrate, to reduce the shrinkage of PVDF due to excess crystallization, to increase the dispersibility of a pigment in a paint, and to obtain good optical properties. The selection of the secondary resin is based largely on the compatibility of the resin with PVDF. Fortunately, PVDF has good compatibility with a few readily available industrial polymers such as acrylic resins and polyvinyl acetates.

[0003] One of the most important characteristics of PVDF coatings is excellent weatherability. A commercial resin known as Acryloid B-44, a copolymer of methyl methacrylate and ethyl acrylate, is commonly used in PVDF coating formulations because the resin provides excellent adhesion and mechanical behavior after mixing with PVDF. A blend of PVDF and Acryloid B-44 was selected for comparison purposes to demonstrate an aspect of the present invention. PMMA is the most compatible polymer for PVDF among acrylic resins which may be attributable to PVDF/PMMA blends having the greatest lowest critical solution temperature among PVDF/PMMA resin blends. The lowest critical solution temperature of PVDF/PMMA is above the melting point of PVDF. Hence, PMMA has been found to provide the best balance of physical properties to a PVDF/PMMA blend.

[0004] Blending polymers has been an important industrial approach towards development of polymeric coating materials. PVDF has been identified as compatible with a few industrial polymers, including polymers of alkyl methacrylate and alkyl acrylates with carbon content on alkyl groups of less than 3. The polymers compatible with PVDF have the common characteristic of high concentrations of C=O groups, particularly on side chains of the carbon polymer. It is known from the prior art that PVDF is compatible with PMMA. See, for example, U.S. Patent 4,770,939. PVDF is also known to be compatible with a blend of PMMA and polyethyl methacrylate. See, U.S. Patent 3,454,518. Extrusion molded products of a PVDF and PMMA thermoplastic resins are also disclosed in the art. See, U.S. Patent Nos. 4,317,860, 4,415,519 and 4,444,826.

[0005] In accordance with one aspect of the present invention, the inventors have found that a resin mixture containing a ratio of PVDF to secondary resin of about 70 to 30 by weight provides the best balance for performance of a coating. Traditionally, an acrylic resin has been the choice as a secondary resin because of its good photo-oxidative resistance. PMMA and PMMA polymers are often used in various PVDF paint formulations. However the technical information found in the literature usually is based on PMMA blends with PVDF, without regard to whether the structure or weight of the PMMA affects the performance characteristics of the PVDF/PMMA blend. The present invention utilizes material comprising PMMA with different molecular weights for PVDF paint characterizations which, surprisingly, affects the physical characteristics of the paint coating, including solvent resistance and gloss retention.

[0006] Based upon film forming mechanism of PVDF coatings, it is anticipated that the primary particle size of PVDF and the molecular weight of the secondary polymer can significantly affect the performance of the final coating. Since PVDF particles undergo plasticization and mixing with solvent and PMMA, respectively, the development of physical properties during the formation of film is a kinetic process. Initially, the solvent swells and solvates PVDF particles, and eventually the solvated PVDF is mixed with PMMA. It has been found that the uniformity of the mixing depends on the molecular weight of the PMMA.

[0007] The present invention relates to effects on the performance of PVDF/PMMA blends of changes in the molecular weight of the PMMA. A typical composition of 70 to 30 of PVDF to acrylic resin is used to demonstrate this invention. The paint coating properties evaluated in the study implemented to demonstrate advantages of the invention include flexibility, hardness, solvent resistance and gloss resistance. The paint coatings were further analyzed for weatherability by QUV weatherometer.

[0008] It is an object of the present invention to develop a material comprising PVDF and PMMA with use of PMMA within a particular molecular weight range which provides a paint coating material with superior physical characteristics, including excellent solvent resistance and gloss retention. Heretofore, it was unknown that a blend of PVDF and PMMA comprising PMMA within a particular molecular weight range affected the physical characteristics of PVDF coatings.

[0009] In the drawing:

Figure 1 is a plot of Inherent Viscosity as a function of Molecular Weight for PMMA, and

Figure 2 is a plot of Percent Gloss Retention as a function of Aging Time for four different samples of PVDF/PMMA blends comprising PMMA of Various molecular weights and Shepard Blue #3 pigment.

[0010] In the following description, the invention is described in terms of a preferred embodiment, but such description should not limit the scope of the invention, which is set forth in the accompanying claims.

[0011] PVDF used to demonstrate aspects of the invention is a homopolymer of vinylidene fluoride. PVDF applications generally involve addition of a secondary polymer to enhance the performance of PVDF coating materials. PVDF is compatible with a wide range of polymers such as polymethacrylates, polyacrylates and polyvinyl acetates containing C=O groups in the ester, amide or ketone forms.

[0012] PMMA is the most widely used secondary polymer for PVDF applications. PMMA has excellent compatibility with PVDF and provides good heat resistance, mechanical properties, weatherability and optical clarity. PMMA used to demonstrate aspects of this invention is a homopolymer of methyl methacrylate.

[0013] In accordance with one aspect of the present invention, it had been found that PVDF coatings with about 30 percent acrylic content in resin compositions provide optimal performance. The present invention is illustrated through use of a PVDF/PMMA blend with 70 weight percent PVDF and 30 weight percent PMMA with the PMMA selected to have different molecular weights. Tests of the present invention demonstrate the effect that the molecular weight of the PMMA has on the PVDF paint coating performance, particularly with respect to solvent resistance and gloss retention.

[0014] Accordingly, blends of PVDF and PMMA with a low molecular weight of about 15,000 grams per mole, a moderate molecular weight of about 120,000 grams per mole and a very high molecular weight of about 1,000,000 grams per mole were prepared and tested for solvent resistance, pencil hardness, gloss-retention, reverse impact, adhesion and accelerated weathering. A blend comprising PVDF and acryloid B-44 resin alloys was also prepared for comparison purposes.

[0015] PMMA obtained from suppliers were characterized by inherent viscosity in N-methylpyrrolidone at 30.5°C in order to ensure the molecular weight effect of PMMA on the performance of a PVDF coating. The inherent viscosity is defined by the following equation:

$$\eta_{inh} = \ln(t/t_0)/C$$

where C is the concentration of PMMA in grams per mole, t and t₀ are flow times of solution and solvent, respectively, in a capillary viscometer. The relationship between the inherent viscosity of PMMA and molecular weight determined by experiment are set forth in Figure 1, and may be expressed by the following equation:

$$\log \eta_{inh} = \log K + a(\log MW)$$

where K and a are equal to 0.022 and 0.57, respectively. Based on this experimental result, the molecular weight of the PMMA provided by the supplier is used in the study described herein to demonstrate aspects of the invention.

Example 1

[0016] PMMA solution with a low molecular weight of 15,000 grams per mole was blended in a pigment to form a uniform dispersion and was then homogenized by a sand mill. For purposes of this experiment, two different pigments were used, Titanium Dioxide and Shepard Blue #3. The PMMA pigment dispersions were added to an amount of PVDF appropriate to formulate a mixture containing, by weight, 70 parts PVDF to 30 parts PMMA. The mixture was then further homogenized by a high speed disperser for 15 minutes and then by glass bead shaker for 15 hours to develop the final paint coating composition. The composition of the paint coatings with PMMA with a molecular weight of 15,000 grams per mole prepared for this study are set forth in Table 1. (See, Experiment Numbers 2 and 6).

[0017] The paint coatings were applied onto aluminum substrates and baked to a peak metal temperature of 465° F in one minute. The dry paint coating on the substrate was tested for solvent resistance, pencil hardness, gloss, reverse impact and adhesion. The testing results are set forth in Table 2. (See, Experiment Numbers 2 and 6).

[0018] The paint coatings prepared with PMMA with a low molecular weight of 15,000 grams per mole were subjected to accelerated QUV weathering tests using UVB-313 lamps and applying standard test method ASTM D 4329-84. The coating was exposed, at intervals, to 8 hours of UV light at 70°C, and 4 hours of condensation at 50°C. The testing interval used to demonstrate this aspect of the invention was every 500 hours for a total testing time of 5,000 hours. The weatherability testing results represented in percentage gloss retention for the paint coating prepared with PMMA with a molecular weight of 15,000 grams per mole and Shepard Blue #3 are described in Figure 2. Similar results were achieved through accelerated QUV weathering tests of paint coatings comprising Titanium Dioxide.

Example 2

[0019] Paint coatings, prepared from PMMA with a moderate molecular weight of 120,000 grams per mole, were formulated using the procedure described in Example 1. The compositions of the paint coatings formulated by use of PMMA with a molecular weight of 120,000 grams per mole prepared for this study are set forth in Table 1. (See, Experiment Numbers 3 and 7).

[0020] The paint coatings were applied onto an aluminum substrate and baked in accordance with the procedure described in Example 1. The dry coating was tested for the criteria listed in Example 1. The testing results are set forth in Table 2. (See, Experiment Numbers 3 and 7).

[0021] The paint coatings prepared with PMMA with a molecular weight of 120,000 grams per mole were subjected to accelerated QUV weathering tests using the equipment and procedures described in Example 1. The coatings were exposed to the same conditions for UV light and condensation for the same time periods, testing intervals and total testing time described in Example 1. The weatherability testing results represented in percentage gloss retention for the paint coating prepared with PMMA with a molecular weight of 120,000 grams per mole and Shepard Blue #3 are described in Figure 2. Similar results were achieved through QUV weathering tests of paint coatings comprising Titanium Dioxide.

Example 3

[0022] Paint coatings, prepared from PMMA with a very high molecular weight of 1,000,000 grams per mole were formulated using the procedure described in Example 1. The composition of the paints formulated by use of PMMA with a molecular weight of 1,000,000 grams per mole prepared for this study are, set forth in Table 1. (See, Experiment Numbers 4 and 8).

[0023] The paint coatings were applied onto an aluminum substrate and baked in accordance with the procedure described in Example 1. The dry coating was tested for the criteria listed in Example 1. The testing results are set forth in Table 2. (See, Experiment Numbers 4 and 8).

[0024] The paint coatings prepared with PMMA with a molecular weight of 1,000,000 grams per mole were subjected to accelerated QUV weathering tests using the equipment and procedures described in Example 1. The coatings were exposed to the conditions for UV light and condensation for the time periods, testing intervals and total testing time described in Example 1. The weatherability testing results represented in percentage gloss retention for the paint coating prepared with PMMA with a molecular weight of 1,000,000 grams per mole and Shepard Blue #3 are described in Figure 2. Similar results were achieved through QUV weathering tests of paint coatings comprising Titanium Dioxide.

Example 4

[0025] Paint coatings, prepared from Acryloid B-44 acrylic resin, were formulated for comparison purposes using the procedure described in Example 1. The composition of the paints formulated by use of Acryloid B-44 acrylic prepared for this study are set forth in Table 1. (See, Experiment Numbers 1 and 4).

[0026] The paint coatings were applied onto an aluminum substrate and baked in accordance with the procedure described in Example 1. The dry coating was tested for the criteria listed in Example 1. The testing results are set forth in Table 2. (See, Experiment Numbers 1 and 4).

[0027] The paint coatings prepared with Acryloid B-44 were subjected to accelerated QUV weathering tests using the equipment and procedures described in Example 1. The coatings were exposed to the conditions for UV light and condensation for the time periods, testing intervals and total testing time described in Example 1. The weatherability testing results represented in percentage gloss retention for the paint coating prepared with Acryloid B-44 resin and Shepard Blue #3 are described in Figure 2. Similar results were achieved through QUV weathering tests of paint coatings comprising Titanium Dioxide.

Table 1

Compositions of PVDF paints used in the study.								
Experiment Number	1	2	3	4	5	6	7	8
PVDF,phr	100	100	100	100	100	100	100	100
Film Forming Resins, phr								
Acryloid B44 acrylic	42.85				42.85			
15,00 MW PMMA		42.85				42.85		
120,000 MW PMMA			42.85				42.85	
1,000,000 MW PMMA				42.85				42.85
Solvent								
Isophorone	180	180	180	180	105	105	105	120
Methyl ethyl ketone	99.96	99.96	99.96	171.40	99.96	99.96	99.96	171.40
Pigment, phr								
TiO ₂	78.60	78.60	78.60	78.60				
Shepard Blue #3					42.85	42.85	42.85	42.85
Solid content. Wt%	44.17	44.17	44.17	38.66	36.57	36.57	36.57	29.94
Pigment/Binder	0.55	0.55	0.55	0.55	0.30	0.30	0.30	0.30
phr - parts per hundred parts PVDF								

Table 2

Molecular weight effect of PMMA on PVDF coating performance.								
Experimental Number	1	2	3	4	5	6	7	8
MEK Double Rubs	110	30	200	20	145	42	166	30
Pencil Hardness	H	H	H	H	H	H	H	H
Adhesion	100%	100%	100%	100%	100%	100%	100%	100%
OT Flexibility	NTO	NTO	NTO	NTO	NTO	NTO	NTO	NTO
Reverse Impact/#80	>80	>80	>80	>80	>80	>80	>80	>80
Gloss-60 deg.	61.00	62.80	56.50	34.00	62.80	55.80	39.40	14.80
DFT/Mils	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85
NTO - No tape off. DFT - Dry film thickness.								

DISCUSSION OF THE RESULTS

[0028] Table 2 shows the effect of molecular weight of PMMA on the performance of typical PVDF coatings. The gloss of the coating decreases with increased molecular weight which is likely the result of a decreased degree of homogeneous mixing and the reduced flowability of the resin mixture. The solvent resistance, measured by methyl-ethyl ketone

("MEK") double rubs, is, however, poorer for blends with both low and high molecular weight PMMA as compared to blends comprising moderate molecular weight PMMA. The results disclose that paint coatings comprising PMMA with a moderate molecular weight of 120,000 grams per mole provide excellent solvent resistance to MEK double rubs. This formulation scored significantly better than the paints formulated with PMMA of very low and very high molecular weights.

[0029] The samples were also analyzed for pencil hardness, adhesion, OT flexibility, reverse impact and dry film thickness. As set forth in Table 2, the differences in molecular weight of the PMMA used in the paint coatings formulated to demonstrate the invention did not dramatically affect these characteristics.

[0030] The gloss retention results after QUV weatherometer tests are described in Figure 2. The gloss of the paint coating comprising Acryloid B-44 resin is reduced gradually upon QUV exposure and ultimately the gloss retention levels off after long exposure. Interestingly, equivalent paint coatings that substitute PMMA for Acryloid B-44 resin do not exhibit significant change in gloss reduction. The percentage of gloss reduction for the coatings studied to demonstrate aspects of the invention can be explained by the differences in photo oxidative degradation of the Acryloid B-44 and PMMA by the QUV exposure conditions. Standard thermogravimetric analyses were applied to the samples which indicate about 70 percent by weight degradation of Acryloid B-44 in paint coatings comprising Acryloid B-44 after 5,000 hours of UV exposure. The paint coatings comprising PMMA, however, exhibited only a small weight percentage of PMMA degradation after 5,000 hours of exposure and the weight percent degradation decreased as the molecular weight of the PMMA in the studied blends increased. Hence, it appears that the most likely significant factor contributing to the decrease of gloss of the paint coatings upon weathering is the generation of free radicals by UV light through photo-oxidation of Acryloid B-44 and PMMA in the blends.

[0031] The experiments disclose that, surprisingly, there is a range of molecular weight for PMMA that can be used in a blend comprising PVDF and PMMA than provides for optimal performance in this regard. The molecular weight range of PMMA disclosed through the experiments is between about 25,000 grams per mole and about 200,000 grams per mole. Previously, it was unknown that there is a preferred molecular weight range of PMMA in blends of PVDF and PMMA.

[0032] While the invention has been described in terms of a preferred embodiment, the scope of the invention is set forth as the following claims.

Claims

1. A coating composition exhibiting enhanced properties, including solvent resistance and gloss retention, comprising a homopolymer of vinylidene fluoride and a homopolymer of methyl methacrylate wherein the polymethyl methacrylate has a molecular weight in the range of about 25,000 grams per mole to about 200,000 grams per mole.
2. The coating composition of claim 1 wherein said polymethyl methacrylate has a molecular weight of about 120,000 grams per mole.
3. The coating composition of claim 1 further comprising solvent.
4. The coating composition of claim 1 wherein said solvent is isophorone or methyl ethyl ketone.
5. The coating composition of claim 1 further comprising pigment.
6. The coating composition of claim 1 wherein said pigment is selected from the group consisting of titanium dioxide and Shepard Blue #3.
7. The coating composition of claim 1 further comprising binder.
8. The composition according to claim 1 for use as a weather resistant coating.
9. Use of the composition according to claims 1-7 for coatings.

Inherent Viscosity of PMMA as a Function of MW

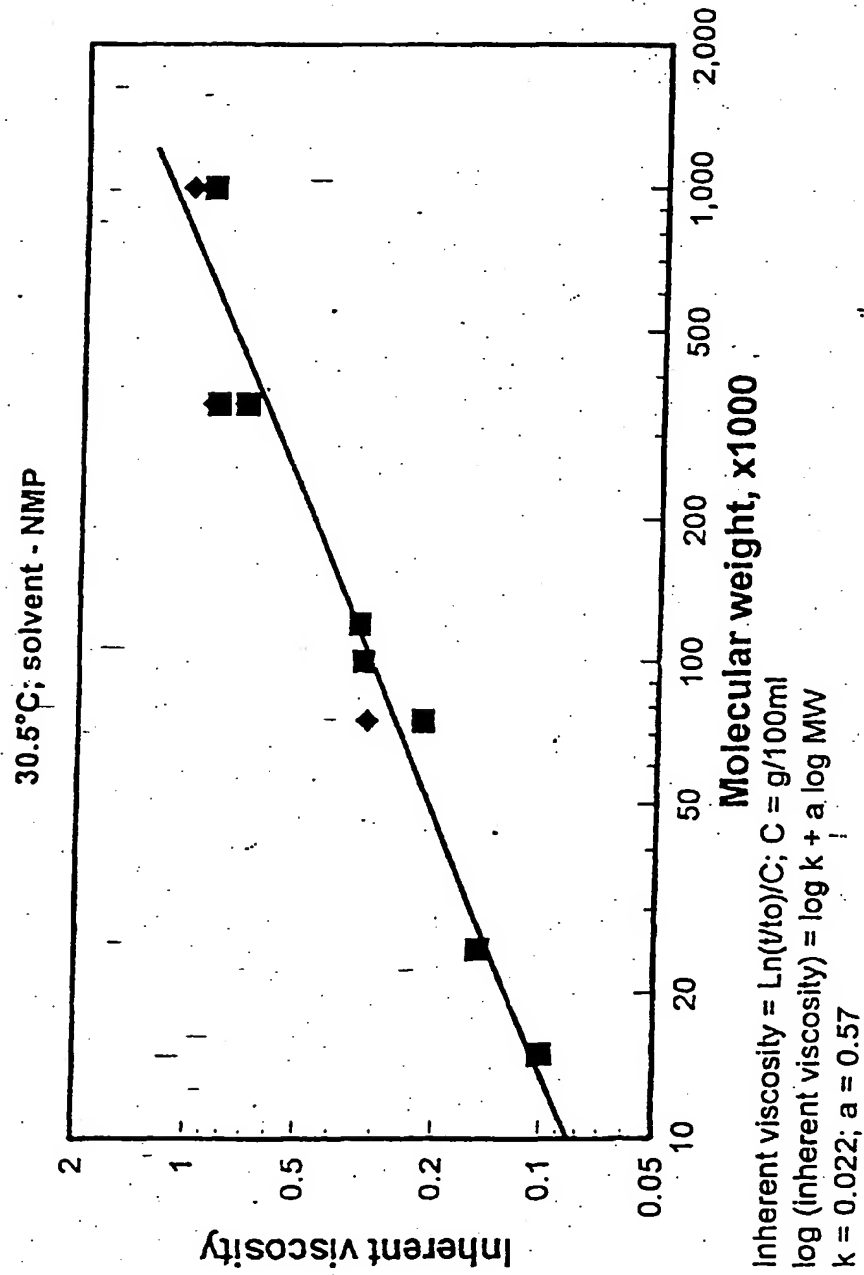


FIGURE 1

WEATHERING OF PVDF/PMMA COATINGS

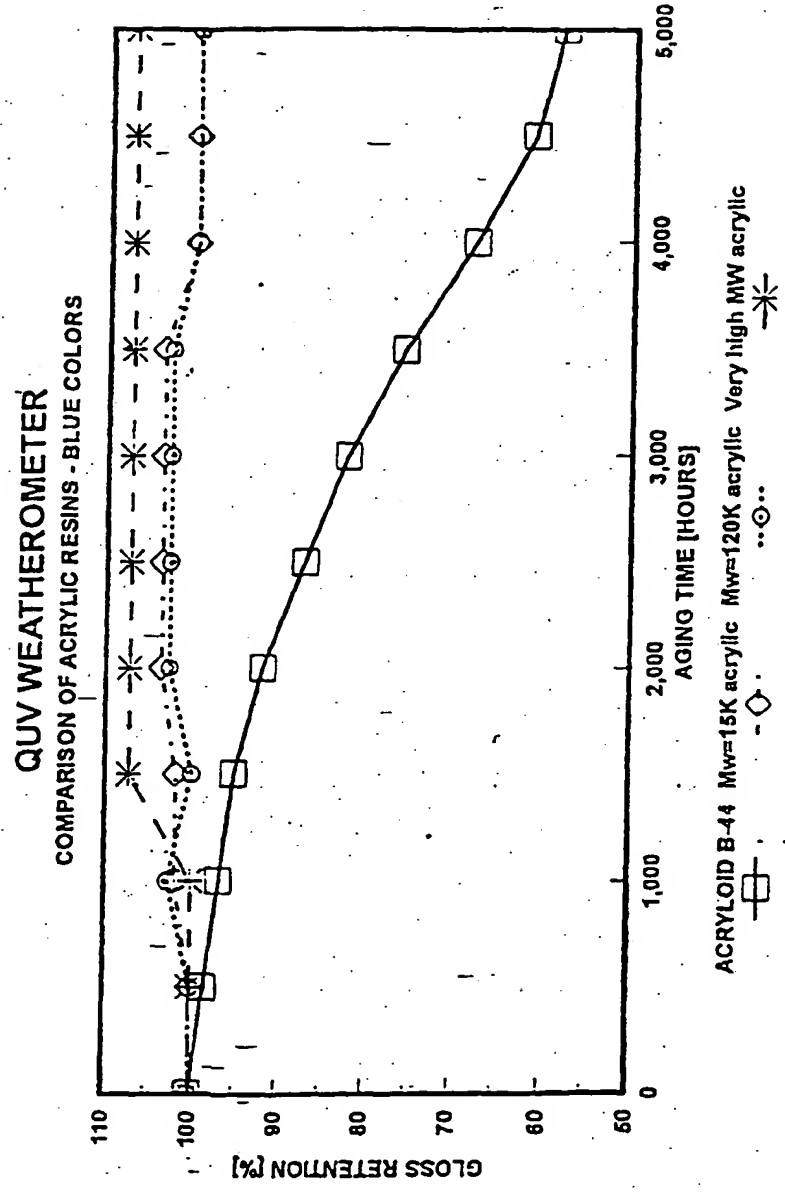


FIGURE 2

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 960 918 A3

(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3:
06.03.2002 Bulletin 2002/10

(51) Int Cl.7: **C09D 133/12, C08K 3/22,**
C09D 127/16

(43) Date of publication A2:
01.12.1999 Bulletin 1999/48

(21) Application number: **99103674.0**

(22) Date of filing: **25.02.1999**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **05.03.1998 US 35256**

(71) Applicant: **AUSIMONT U.S.A., Inc.**
Thorofare, New Jersey 08086 (US)

(72) Inventors:
• **Lin, Shioh-Ching**
Lawrenceville, New Jersey 08648 (US)
• **Kamsler, Craig**
North Brunswick, New Jersey 08902 (US)
• **Argasinski, Karol**
Sicklerville, New Jersey 08081 (US)

(74) Representative: **Sama, Daniele, Dr. et al**
Sama Patents, Via G.B. Morgagni, 2
20129 Milano (IT)

(54) **Polyvinylidene fluoride weather resistant coating compositions including polymethyl methacrylate**

(57) A coating composition blend comprising PVDF and PMMA with the PMMA having a molecular weight within the range of about 25,000 grams per mole to about 200,000 grams per mole that results in a blend of

PVDF and PMMA with excellent physical characteristics, including solvent resistance and gloss retention.

EP 0 960 918 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 10 3674

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (InCLIS)
X	TOURNUT C ET AL: "COPOLYMERS OF VINYLIDENE FLUORIDE IN COATINGS" SURFACE COATINGS INTERNATIONAL, WEMBLEY, GB, vol. 78, no. 3, 1995, pages 99-100, 102-103, XP000869833 ISSN: 0030-1337 * table 2 *	1	C09D133/12 C08K3/22 C09D127/16
X	US 5 132 164 A (MORIYA YOSHIHISA ET AL) 21 July 1992 (1992-07-21) * claims; examples *	1	
X	EP 0 483 887 A (FINA RESEARCH) 6 May 1992 (1992-05-06) * claims; examples *	1,5	
			TECHNICAL FIELDS SEARCHED (InCLIS)
			C09D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 7 January 2002	Examiner Schueler, D
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03 82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 10 3674

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

07-01-2002

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
US 5132164	A	21-07-1992	JP	2151436 A	11-06-1990
			JP	2739976 B2	15-04-1998
			US	5256472 A	26-10-1993
EP 0483887	A	06-05-1992	GB	2194539 A	09-03-1988
			AT	77290 T	15-07-1992
			EP	0483887 A2	06-05-1992
			GR	3034703 T3	31-01-2001
			AT	195093 T	15-08-2000
			DE	3752320 D1	07-09-2000
			DE	3752320 T2	08-02-2001
			DE	3779841 D1	23-07-1992
			DE	3779841 T2	24-12-1992
			EP	0259290 A2	09-03-1988
			ES	2032868 T3	01-03-1993
			ES	2149756 T3	16-11-2000
			GR	3004956 T3	28-04-1993
			US	4770939 A	13-09-1988

EPO FORM P4163

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82